

# RSC Applied Polymers

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Chen, Z. Yin, Z. Chen and C. Pan, *RSC Appl. Polym.*, 2025, DOI: 10.1039/D5LP00223K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

## ARTICLE

# Electrical and Thermoelectric Properties of a Poly(3-(2-octyldodecyl)thiophene)/Poly(3-octylthiophene)/2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane Polymer Blend Doping System

Viscoelastic

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Roujun Chen,<sup>a,b,1</sup> Zijian Yin<sup>a,1</sup>, Zhongming Chen<sup>c,\*</sup>, and Chengjun Pan<sup>a,\*</sup>

Organic thermoelectric materials have attracted significant research interest due to their unique advantages. Chemical doping serves as a key strategy for enhancing the thermoelectric performance of conductive polymers by modulating their electronic structures and physical properties. In this study, we investigated the electrical and thermoelectric properties of blend-doped composites comprising poly(3-(2-octyldodecyl)thiophene) (P3ODT, with branched alkyl side chains) and poly(3-octylthiophene) (P3OT, with linear alkyl side chains), doped with 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane (F<sub>4</sub>-TCNQ). The results demonstrated that incorporating P3ODT enhanced the flexibility and surface quality of the material. As the proportion of P3ODT increased in the test groups, the number of conductive complexes decreases, leading to a reduction in electrical conductivity. But the Seebeck coefficient of the blend-doped material initially rose continuously, reaching a maximum of 62.67  $\mu\text{V K}^{-1}$  due to optimized carrier energy filtering while it declined when the P3ODT:P3OT ratio reached 4:6. Notably, despite the lower conductivity, the thermoelectric performance peaked at a P3ODT:P3OT ratio of 1:9, achieving a power factor (PF) of 0.69  $\mu\text{W m}^{-1} \text{K}^{-2}$ . Regarding the doping mechanism, F<sub>4</sub>-TCNQ effectively induced the aggregation of P3OT and the generation of polarons/bipolarons. However, its doping reaction with P3ODT was limited, likely due to the steric hindrance caused by bulky alkyl side chains of P3ODT. Nevertheless, the alkyl side chains enhanced carrier mobility through backbone planarization which compensated for the reduced carrier concentration and conductivity. These findings suggested that blending P3ODT as a second conjugated polymer with tailored side chains can offer an effective strategy to improve the thermoelectric properties of flexible organic materials, providing valuable molecular design principles for performance optimization.

## Introduction

Thermoelectric (TE) materials are recognized for their ability to directly convert thermal energy, such as solar energy and waste heat, into electrical energy, making them a sustainable and strategically important class of materials<sup>1</sup>. While inorganic TE materials exhibit excellent thermoelectric properties and high conversion efficiencies<sup>2,3</sup>, their applications are constrained by several drawbacks, including toxicity, high production costs, and mechanical brittleness. To address these challenges, flexible TE materials have gained prominence as promising alternatives, offering advantages such as abundant raw materials, lightweight design, mechanical flexibility, solution

processability, and low-cost fabrication<sup>4,5</sup>. Among these, conjugated polymers, –a key subset of flexible TE materials, are characterized by conjugated repeating units with alternating single and double bonds<sup>6</sup>. This structural feature allows  $\pi$ -electron delocalization along the polymer backbone, creating extended electron distribution pathways and intrinsic electrical conductivity<sup>7,8</sup>. Representative examples include polypyrrole<sup>9</sup>, polyaniline<sup>10</sup>, polyfluorene, polyindole, and polythiophene<sup>11,12</sup>. Crucially, their reversible doping behavior and doping range of these polymers significantly enhance the charge conductivity along the polymer backbone, which is a key factor in their preference for thermoelectric applications.

The solubility of conjugated polymers is governed by their side-chains architecture, particularly the size and the length of alkyl side chains, which critically influence material properties and device performance<sup>13–15</sup>. These polymers are categorized as viscoelastic conjugated polymers (VE-CPs), characterized by a rigid  $\pi$ -conjugated backbone paired with flexible side-chain structures. The side chains act as "internal plasticizers", balancing mechanical flexibility with electronic functionality. To systematically tune these properties, researchers have employed side-chain engineering strategies. For instance, Pan et al.<sup>16</sup> modulated the alkyl-to- $\pi$  ratio in polyfluorene

<sup>a</sup> College of Material Science and Engineering, State Key Laboratory of Fine Chemicals, Shenzhen University, Shenzhen 518060, P. R. China. [pancj@szu.edu.cn](mailto:pancj@szu.edu.cn)

<sup>b</sup> Key laboratory of Resources Environmental and Green Low Carbon Processes in East Guangdong, School of Chemistry and Environmental Engineering, Hanshan Normal University, Chaozhou, 521041.

<sup>c</sup> School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China

<sup>1</sup> These authors contributed equally to this work.

† Footnotes relating to the title and/or authors should appear here.

Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



derivatives via "alkyl- $\pi$ " engineering, enabling precise control over the polymer phase behavior—transitioning from fluid to a viscoelastic and ultimately solid state. Similarly, Akira et al.<sup>17</sup> designed poly(phenylene-benzothiadiazolyl-bis(thiophene)) as the backbone and elongated its dendrimer-like alkyl side chains. This modification improved the polymer's mechanical stability at room temperature, inducing a solvent-free transition from a brittle glassy state to a viscoelastic state without compromising its fluorescence properties. Collectively, these studies demonstrate that branching alkyl side chains on  $\pi$ -conjugated backbones (e.g., in poly(thiophene)) enhance the mechanical robustness of VE-CPs, a critical advancement for developing durable, high-performance organic thermoelectric materials.

The thermoelectric properties of materials are typically quantified by the power factor ( $PF = S^2 \sigma$ ), where  $S$  is the Seebeck coefficient and  $\sigma$  is the electrical conductivity. At a fixed temperature, both  $S$  and  $\sigma$  are dependent on the energy difference between the Fermi energy ( $E_F$ ) and the transport energy ( $E_{tr}$ ), expressed as  $S \propto (E_F - E_{tr})/T$  and  $\sigma \propto \exp[(E_F - E_{tr})/T]$ . Here,  $E_F$  is modulated by carrier concentration and electronic states, while  $E_{tr}$  corresponds to the energy range within the density of states (DOS) that contributes to charge transport. To optimize PF, researchers employ chemical doping to adjust  $E_F$  by increasing intrinsic carrier concentration, thereby balancing  $S$  and  $\sigma$ .<sup>18,19</sup> For example, Chabinyk et al.<sup>20</sup> systematically studied the doping effects of fluoroalkyltrichlorosilanes (FTS) and 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane ( $F_4$ -TCNQ) on poly(3-hexylthiophene) (P3HT) and poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTC14). Their work demonstrated that optimizing dopant selection enhances electrical conductivity and PF by up to 200-fold and 20-fold, respectively, in these polythiophene derivatives.

$F_4$ -TCNQ is particularly effective due to its ability to induce ground-state charge transfer with conjugated polymers, generating polarons and bipolaron that improve charge transport. For instance, in doped P3HT, electrons transfer from the polymer's highest occupied molecular orbital (HOMO) to the dopant's lowest unoccupied molecular orbital (LUMO), achieving integer charge transfer.<sup>21,22</sup> Building on this, David Kiefer et al.<sup>23</sup> reported that double doping with  $F_4$ -TCNQ produces a high doping efficiency of 170% at low concentrations, as a large fraction of generated carriers participate in conduction. These findings highlight  $F_4$ -TCNQ and its derivatives as versatile dopants for conjugated polymers, enabling efficient charge modulation at minimal doping levels—a critical strategy for advanced organic thermoelectrics.

The ionization of dopants can significantly alter the DOS within conjugated polymers, which plays a pivotal role in the charge and energy transport properties of organic TE materials. However, at high doping concentrations, this process often induces disordered surface morphology in doped polymers, which degrades charge transport pathways and ultimately limits TE performance optimization.<sup>24,25</sup> To resolve this trade-off between doping level and morphology, researchers have developed polymer blending strategies that synergize complementary properties of distinct conjugated polymers. For

instance, Mahan and Sofo<sup>26</sup> proposed a theoretical framework for blend systems composed of two polymers with differing energy landscapes. Their model incorporates a triangular transport distribution above the  $E_F$ , demonstrating that such blends enhance charge transport by creating two distinct DOS profiles. Experimentally, Zuo et al.<sup>27</sup> validated this concept by fabricating binary blends of conjugated polymers with mismatched HOMO energy level. By adjusting the blend ratio, they observed a systematic shift in the  $E_{tr}$  toward the DOS of the dominant polymer. This approach enables precise control over the Seebeck coefficient while maintaining high electrical conductivity, thereby optimizing the PF and advancing TE performance in blended systems.

Organic thermoelectric materials offer compelling advantages over inorganic counterparts, including resource sustainability, mechanical flexibility, solution processability, and low-cost fabrication. The TE performance of conjugated polymers can be optimized by enhancing electrical conductivity through chemical doping, with the carrier concentration being highly dependent on the doping efficiency. Thus, strategic selection of dopant type and concentration is significant for maximizing TE properties. Building on this principle, we employed a viscoelastic conjugated polymer with nonpolar 3-(2-octyldodecyl) thiophene side chains using an "alkyl- $\pi$ " engineering strategy. This polymer was blended with poly(3-octylthiophene) P3OT at varying weight ratios and molecularly doped with  $F_4$ -TCNQ to systematically investigate TE performance trends in the blended systems. This study aims to elucidate the response of the novel blended polymers to chemical doping and to provide a theoretical basis for the optimization of future thermoelectric material performance.

## Experimental Sections

### Materials

Sodium thiosulfate ( $Na_2S_2O_3$ , 98%) and [1,3-bis(diphenylphosphino)propane] nickel(II) chloride ( $Ni(dppp)Cl_2$ ,  $C_{27}H_{26}Cl_2NiP_2$ , 98%) were purchased from Anhui Zesheng Technology Co., Ltd. N-Bromosuccinimide (NBS,  $C_4H_4BrNO_2$ , 98%), isopropylmagnesium chloride ( $iPr-MgCl$ ,  $C_3H_7ClMg$ , 98%), and 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane ( $F_4$ -TCNQ,  $C_{12}F_4N_4$ , 97%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Chloroform ( $CHCl_3$ , A.R.) and hydrochloric acid (HCl, C.R.) were sourced from Sinopharm Chemical Reagent Co., Ltd. and Damao Chemical Reagent Factory, respectively. All solvents, including anhydrous-grade reagents, were supplied by Anhui Zesheng Technology Co., Ltd.

### Synthesis

**2,5-Dibromo-3-octylthiophene (S1) and 2,5-Dibromo-3-(2-octyldodecyl)thiophene (S2).** In a double-necked flask (Flask A), 3-octylthiophene (1.5 g, 1.0 eq.) was dissolved in anhydrous THF (20 mL) under a nitrogen atmosphere. Concurrently, N-bromosuccinimide (NBS, 2.07 g, 2.1 eq.) was dissolved in anhydrous THF (30 mL) in a separate double-necked flask (Flask B). The NBS solution was then slowly added to Flask A via



syringe under an ice-water bath, and the reaction mixture was stirred at 0 °C for 30 minutes. After removing the ice bath, the reaction was allowed to proceed at room temperature in the absence of light for 6 hours. Upon completion, the mixture was extracted with n-hexane and washed with a 10% aqueous sodium thiosulfate solution. The organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated by rotary evaporation to afford the crude product. Purification via column chromatography (n-hexane as eluent) yielded S1 as a colorless transparent-oily product with an 87% yield. For the synthesis of S2, an identical procedure was employed using 3-(2-octyldodecyl) thiophene (2 g, 1.0 eq.) and NBS (2.15 g, 2.2 eq.), yielding S2 as a colorless transparent-oily product in 84% yield.

**Poly(3-alkylthiophene) (P3ODT, P3OT) with different alkyl side chains.** Poly(3-alkylthiophenes) were synthesized via catalyst transfer polycondensation (CTP), with S1 and S2 employed in a catalyst ratio of 100:1 and 150:1, respectively, for the preparation of poly(3-octylthiophene) (P3OT) and poly(3-(2-octyldodecyl)thiophene) (P3ODT). The synthesis procedure for P3ODT is detailed below as a representative example:

In a nitrogen atmosphere, S2 (500 mg, 1 eq.) was vacuum-dried at 60 °C for 4 h to remove residual moisture. The dried monomer was then dissolved in anhydrous THF (10 mL) in a double-necked flask (Flask C), and the solution was degassed via vacuum heating at 40 °C for 10 min with vigorous stirring. The Flask C was cooled to 0 °C in an ice-water bath, and i-PrMgCl (0.95 mmol, 0.98 eq.) was added dropwise via syringe. The reaction mixture was shielded from light with aluminum foil and stirred at room temperature for 30 min to ensure complete monomer activation. In parallel, the catalyst  $\text{Ni}(\text{dppp})\text{Cl}_2$  (0.0128 mmol, 0.0067 eq.) was loaded into a double-necked flask (Flask D) under nitrogen and suspended in anhydrous THF (2 mL). This catalyst suspension was then slowly injected into Flask C, triggering an immediate color change to orange-red accompanied by bright orange-red fluorescence under UV light (365 nm), indicative of polymer chain propagation. The reaction was maintained at 45 °C for 12 h under continuous stirring. After cooled to room temperature, the polymerization was quenched by adding 1 M HCl (5 mL). The crude product was extracted by partitioning the mixture between deionized water (20 mL) and chloroform (30 mL). The organic layer was isolated, dried over anhydrous  $\text{MgSO}_4$ , filtered, and concentrated via rotary evaporation. The resulting residue was dissolved in chloroform (5 mL) and precipitated into methanol (50 mL) in centrifuge tube. The suspension was centrifuged at 6000 rpm for 10 min, and supernatant was decanted to removed unreacted monomers and oligomers. This precipitation-centrifugation cycle was repeated three times. The final polymer-rich precipitate was vacuum-dried at 40 °C for 12 h, yielding 320 mg (66%) of P3ODT as a viscous orange-red solid.

**Preparation of P3ODT/P3OT/ $\text{F}_4\text{-TCNQ}$  viscoelastic polymer blend solutions and films.** P3ODT/P3OT blend solutions were prepared by mixing the two polymers in mass ratio of 0:10, 1:9, 2:8, 3:7, and 4:6 (P3ODT:P3OT). Each mixture was dissolved in anhydrous o-dichlorobenzene (ODCB) at a concentration of 5

mg  $\text{mL}^{-1}$  and stirred at 60 for 2 h to ensure complete dissolution, resulting in homogeneous orange-red solutions. Separately,  $\text{F}_4\text{-TCNQ}$  was dissolved in chloroform at a concentration of 1 mg  $\text{mL}^{-1}$ . Chloroform was selected as the dopant solvent due to its lower boiling point (61 °C) compared to ODCB (180 °C), enabling precise control over solvent evaporation during film formation to minimize defects.

Then 1 mL of each P3ODT/P3OT (0:10, 1:9, 2:8, 3:7, 4:6) blend solution was combined with the  $\text{F}_4\text{-TCNQ}$  solution, achieving a doping level of  $\text{F}_4\text{-TCNQ}$  were 20 wt%, 18 wt%, 16 wt%, 14 wt%, 12 wt%, respectively. Additional chloroform was added to standardize the volume of each blend solution. These doped blend solutions were sonicated for 1 h to ensure uniform dispersion of  $\text{F}_4\text{-TCNQ}$  and molecular-level doping of the polymer matrix. The 20 wt% doping level was selected based on prior optimization studies, which indicated this concentration maximizes charge-transfer efficiency between  $\text{F}_4\text{-TCNQ}$  and P3OT while avoiding phase separation. Finally, 100  $\mu\text{L}$  of each doped blend solutions were carefully drop-cast onto 1 cm  $\times$  1 cm glass substrates using a pipette. The films were dried under ambient conditions (25 °C, 45% relative humidity) in a dark environment for 24 h to prevent photo-oxidation and ensure controlled solvent evaporation. This process yielded flexible P3ODT/P3OT/ $\text{F}_4\text{-TCNQ}$  blend films with varying mass ratios.

## Results and discussion

### Characterization of synthetic polymers

In this study, monomers S1 and S2 were synthesized via bromination, followed by the preparation of P3OT and P3ODT through catalyst-transfer polycondensation. The structures of these polymers were confirmed by  $^1\text{H}$  NMR spectroscopy (Fig. S1-S4), while their molecular weights and dispersity were determined via gel permeation chromatography (Fig. S5 and Table S1). Both polymers exhibited molecular weights consistent with synthetic targets, with closely matched values between P3OT and P3ODT. TGA confirmed the excellent thermal stability of P3OT and P3ODT with 5% weight loss up to 409 °C and 424 °C, well beyond our measurement range. FTIR analysis (Fig. 1A) revealed a distinct cyanide band at  $\sim 2225\text{ cm}^{-1}$  for pure  $\text{F}_4\text{-TCNQ}$  manifested. In contrast, the undoped polymers exhibited no discernible absorption peak in this region. After doping, the blended P3OT/ $\text{F}_4\text{-TCNQ}$  system displayed a redshifted absorption peak at  $\sim 2191\text{ cm}^{-1}$  ( $\Delta\nu \approx 34\text{ cm}^{-1}$ , Fig. 1B), indicative of integer charge transfer between P3OT and  $\text{F}_4\text{-TCNQ}$ , consistent with the formation of  $\text{F}_4\text{-TCNQ}^{-1}$  species<sup>22,28,29</sup>. Conversely, doped P3ODT exhibited a significantly smaller shift ( $\Delta\nu \approx 17\text{ cm}^{-1}$ ), approximately half the magnitude observed for P3OT, suggesting partial charge transfer involving electron sharing across multiple sites. This distinction implies complete doping in P3OT but incomplete doping in P3ODT under these conditions. Furthermore, the absence of residual peaks at  $2225\text{ cm}^{-1}$  after doping indicates full participation of  $\text{F}_4\text{-TCNQ}$  in both systems, although with differing charge-transfer efficiencies.

### XRD spectroscopy





The crystalline structures of P3OT, P3ODT and their doped blends were analyzed via X-ray diffraction (XRD, Fig. 2). As shown in Fig. 2A, P3OT displayed sharp diffraction peaks at  $4.2^\circ$ ,  $8.5^\circ$ ,  $12.9^\circ$  and  $23.4^\circ$ , as well as a broad diffuse peak at  $18.4^\circ$ , confirming its crystalline nature. In contrast, P3ODT exhibited no distinct diffraction peaks but a prominent diffuse halo at  $20^\circ$ , indicative of an amorphous structure lacking long-range order. This disparity may be attributed to long-branched side chain of P3ODT, restricting close backbone stacking. For blended polymers (Fig. 2B), the (100) peak position remained unaltered, but its intensity decreased, reflecting reduced crystallinity due to blending. After doping, the (100) peak of P3OT shifted by  $3.8^\circ$  (from  $4.2^\circ$  to lower angles, Fig. 2C and Table S2), accompanied by an increase in interplanar spacing from 2.043 nm to 2.298 nm. This lattice expansion and peak broadening suggest doping-induced disordering, likely resulting from the destabilization of

The structural and electronic changes in P3OT/P3ODT/ $F_4$ -TCNQ films were probed using UV-vis-NIR spectroscopy. Raman data (Fig. S7) revealed a broadening of the  $\alpha=\beta$  stretching vibrational peak to  $1448.22\text{ cm}^{-1}$ , indicative of a shift in the film structure toward a more disordered state. Increasing the P3OT/P3ODT ratio induced a progressive redshift in these peaks, consistent with a transition from a benzenoid to quinoid backbone conformation<sup>30,31</sup>, implying the formation of bipolaron. UV-vis-NIR analysis further elucidated this doping effects. As Fig. 3A illustrated, the undoped P3OT showed a  $\pi-\pi^*$  transition peak in the solvation state (s-P3OT) at approximately 450 nm, while a novel aggregation state absorption peak (nw-P3OT) emerged at 584 nm following doping, indicating that  $F_4$ -TCNQ promoted the polymer chain planarization. The sharp absorption peak at 391 nm was the  $F_4$ -TCNQ produced after accepting electrons<sup>32</sup>. The reduction in the absorption peak of

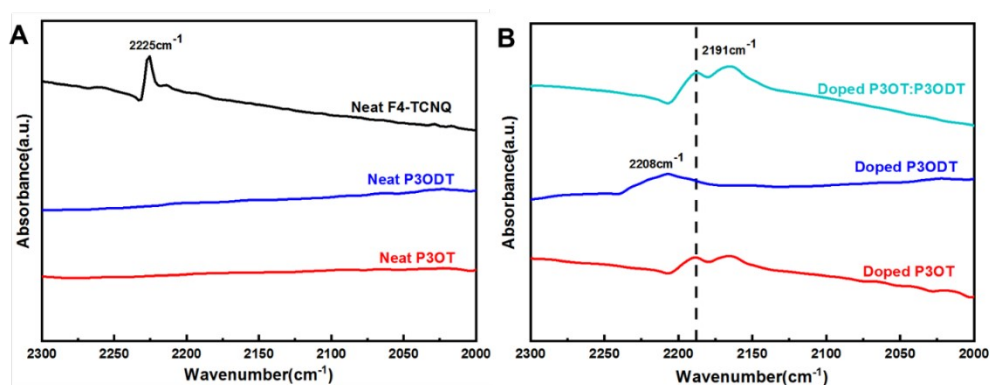


Fig. 1 (A) Infrared spectra of P3OT, P3ODT,  $F_4$ -TCNQ. (B) Infrared spectra of P3OT, P3ODT, P3ODT/P3OT blends in the doped state.

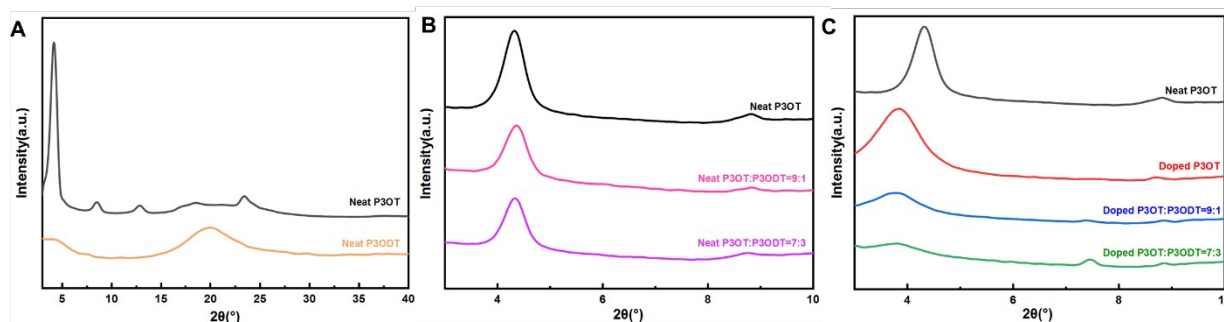


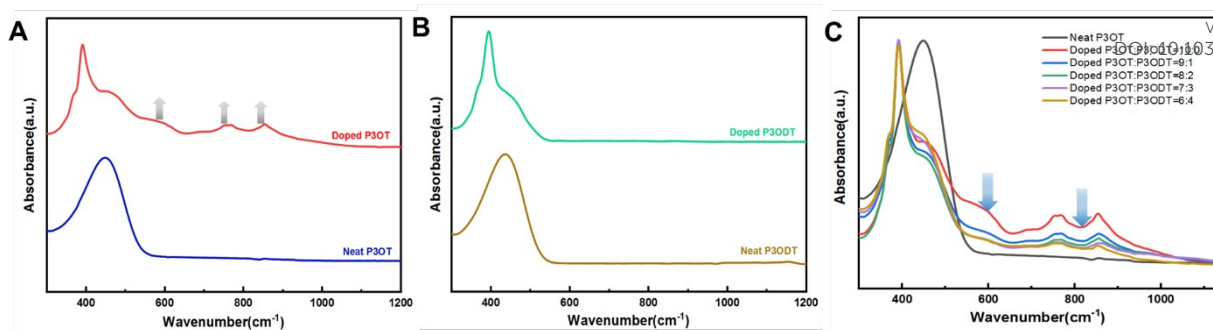
Fig. 2 (A) XRD diffraction pattern of P3OT and P3ODT. (B) XRD diffraction pattern of different blending ratio polymers. (C) XRD diffraction pattern of polymer/ $F_4$ -TCNQ doped materials with varying blending ratios.

polaritons and lattice distortion. As the proportion of the blending phase P3ODT increased, the (100) peak broadened and grain size decreased, reaching a minimum of 4.450 nm at a 3:7 P3ODT:P3OT ratio (Fig. 2C). These trends indicated that the interaction between P3ODT and P3OT lowered the crystallinity of the material to some extent. Compared to doped P3OT without blending, the doped P3ODT: P3OT material possessed a larger layer spacing, implying that the incorporation of P3ODT handicapped the interlayer stacking of the polymers, resulting in some phase separation.

#### UV-vis-NIR spectroscopy

doped P3OT at  $\sim 450\text{ nm}$  was likely due to the electron transfer from the ground state of P3OT to  $F_4$ -TCNQ. This process diminished the internal electron density within P3OT, which in turn directly reflected the significant impact of the dopant  $F_4$ -TCNQ on the electronic structure of P3OT<sup>33,34</sup>. The absorption peaks at  $\sim 766\text{ nm}$  and  $\sim 855\text{ nm}$  implied the formation of polaron/bipolaron in the doped P3OT, which aligned with the results shown by Raman spectroscopy, confirming charge carrier generation.





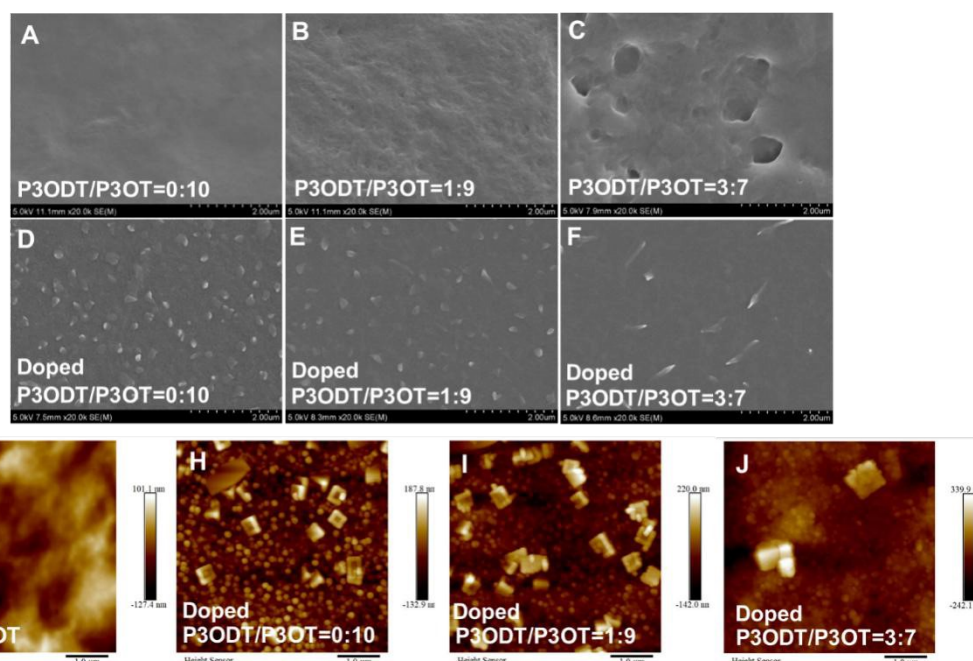
**Fig. 3** (A) UV-vis-NIR spectra of the intrinsic and doping states of P3OT. (B) UV-vis-NIR spectra of intrinsic and doping states of P3ODT. (C) UV-vis-NIR spectra of P3ODT/P3OT doped states at different blending ratios.

In contrast, doped P3ODT (Fig. 3B) retained its intrinsic  $\pi$ - $\pi^*$  transition absorption peaks at 435 nm. Combined with Fig. 1 B, although the doped P3ODT exhibits an electron-transfer shoulder and an F<sub>4</sub>-TCNQ<sup>-</sup> absorption peak, the P3ODT<sup>+</sup> polariton was not formed resulting from the partial charge-transfer mechanism. This incomplete doping interaction was directly attributed to the steric hindrance imposed by the bulky size of the alkane-branched chain of P3ODT, which hindered interaction with the F<sub>4</sub>-TCNQ, resulting in the formation of aggregates being prevented. Further supporting the limited interaction between P3ODT and F<sub>4</sub>-TCNQ, Fig. 3C showed that the polarons/bipolarons peaks of P3OT declined with the augmentation of P3ODT content which suggested that P3ODT impeded the interaction between P3OT and F<sub>4</sub>-TCNQ, leading to a reduction in the carrier concentration. This phenomenon was likely due to the viscoelastic P3ODT, which might have wrapped around P3OT, hindering the reaction with F<sub>4</sub>-TCNQ.

#### Microscopic morphology studies

The surface morphology of P3OT films and P3ODT/P3OT blend films were examined using scanning electron microscopy (SEM)

and atomic force microscopy (AFM). The results (Fig. 4A) showed that the surface of pure P3OT films was smooth and uniform without significant aggregation. However, with the increase of P3ODT content (Fig. 4B-C), the surface of the blended film became rough, and aggregation occurred. When the ratio of P3ODT/P3OT reached 3:7, island-like structures and voids emerged, which could be attributed to the poor mixing of P3OT and P3ODT in the solvent-free state, leading to phase separation and film deterioration. The introduction of the molecular dopant F<sub>4</sub>-TCNQ led to the formation of particles on the unblended P3OT film (Fig. 4D), thus indicating the creation of conductive complexes between P3OT and F<sub>4</sub>-TCNQ. Notably, as the proportion of P3ODT rose, higher P3ODT ratios in blended systems suppressed particle density (Fig. 4E-F), signifying a reduction in the number of conductive complexes. As AFM illustrated (Fig. 4G), island-like structures could be observed in pure P3OT films via AFM, while the absence of such structures in SEM images. After doping, the island structure was diminished while the number of conductive complexes was augmented, thereby enhancing the grain boundary density of the doped film<sup>16</sup> (Fig. 4H-J). Conversely, P3ODT-blended films



**Fig. 4** (A-C) SEM images of different ratios of blending films. (D-F) SEM images of different ratios of blend-doped films. (G-J) AFM images of neat P3OT film. (K-J) AFM images of different ratios of blend-doped films.



lacked such islands and exhibited lower particle concentrations, consistent with SEM observations. In summary, the interaction of P3ODT/P3OT with F<sub>4</sub>-TCNQ enhanced the film quality, whereas the blended with P3ODT was associated with an improvement in carrier mobility.

### Thermoelectric properties

Fig. 5 demonstrated that the thermoelectric properties of the P3ODT/P3OT/F<sub>4</sub>-TCNQ viscoelastic polymer blended films depended on the blend ratio at room temperature. All blends displayed positive Seebeck coefficients, confirming p-type (hole-dominated) charge transport. At the blending ratio of 3:7, the Seebeck coefficients reached a maximum value of 62.67  $\mu\text{V K}^{-1}$ . This was attributed to the incorporation of the second phase (P3ODT), which improved the material carrier mobility while optimizing the surface morphology of the film. However, the further increase in the P3ODT ratio instead made Seebeck coefficients decrease, probably due to the large degree of separation of the two phases, resulting in the blockage of carrier mobility. The conductivity of the P3ODT/P3OT/F<sub>4</sub>-TCNQ blend films exhibited a declining trend with the increase in the P3ODT ratio. This phenomenon was explained by the inhibition of P3ODT on the formation of conductive complexes, consequently reducing the carrier concentration of the films. The power factor (PF) reached its maximum value (0.697  $\mu\text{W m}^{-1}\text{K}^{-2}$ ) at a 1:9 P3ODT:P3OT ratio, indicating that although the P3ODT phase lowered the carrier concentration, the

regions, directly validating the observed electrical and thermoelectric behavior.

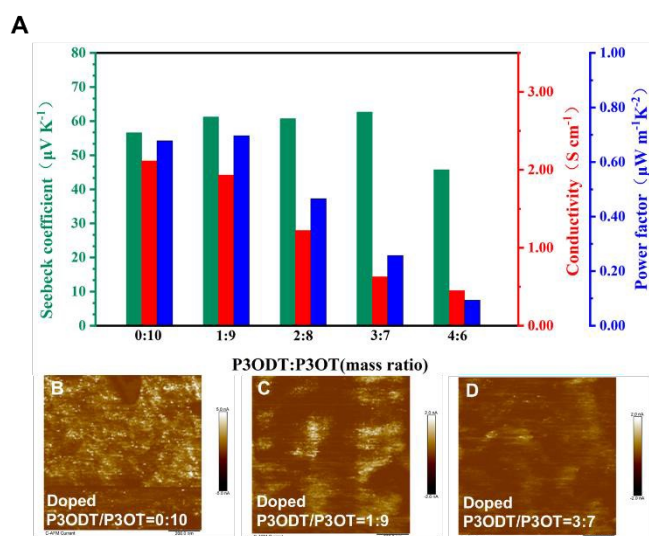
DOI: 10.1039/D5LP00223K

Hall effect tests were performed on P3ODT/P3OT/F<sub>4</sub>-TCNQ doped films to quantify carrier mobility ( $\mu$ ) and carrier concentration ( $n$ ). The results of these tests were shown in Table 1. Theoretically, the Seebeck coefficient was negatively correlated with the carrier concentration and positively correlated with the carrier mobility<sup>35,36</sup>. The conductivity ( $\sigma$ ) was determined by the carrier mobility ( $\mu$ ) and the carrier concentration ( $n$ ), and the relationship could be expressed as  $\sigma = ne\mu$ . Consistent with this framework, doped P3OT exhibited a high  $n$  value ( $1.79 \times 10^{20} \text{ cm}^{-3}$ ), correlating with its

Sample	$\mu (\text{cm}^2 \text{V}^{-1} \text{S}^{-1})$	$n (\text{cm}^{-3})$	$\sigma (\text{S cm}^{-1})$
Doped P3OT	$1.41 \times 10^{-1}$	$1.79 \times 10^{20}$	4.0348
Doped P3OT:P3ODT=9:1	$1.81 \times 10^{-1}$	$1.35 \times 10^{20}$	3.9099
Doped P3OT:P3ODT=7:3	$38.2 \times 10^{-1}$	$4.80 \times 10^{18}$	2.9366

elevated conductivity. As P3ODT content increased, both  $n$  and  $\sigma$  decreased monotonically (Table 1), attributable to bulky side chains of P3ODT sterically hindering F<sub>4</sub>-TCNQ access to P3OT backbones, thereby suppressing conductive complex formation. However, a modest enhancement in carrier mobility was observed in blend films with an elevated proportion of P3ODT. This phenomenon was hypothesized as the wrapping of the branched alkyl side chains of P3ODT, which resulted in a smoother polymerization backbone. This finding offered further validation to the assertion that the reduction of grain boundary density in the AFM images (Fig. 4 I-K) could enhance carrier mobility to a certain extent.

**Table 1** Carrier mobility, carrier concentration and conductivity of blend-doped materials with different blending ratios.



**Fig. 5** (A) Thermoelectric properties of P3ODT/P3OT/F<sub>4</sub>-TCNQ films with different blending ratios. (B-D) C-AFM images of P3ODT/P3OT/F<sub>4</sub>-TCNQ films with different blending ratios.

increase in carrier mobility could compensate for this decrease so that the PF value appeared ascending tendency. This also revealed that the introduction of another conjugated polymer to the conjugated polymer matrix in an appropriate amount would enhance the thermoelectric properties of the blend materials. The Conducting atomic force microscope (C-AFM) corroborated these trends (Fig. 6). Films with a 1:9 P3ODT:P3OT ratio showed optimal conductivity distribution (balanced brightness), while higher P3ODT content reduced conductive

### Conclusions

In this study, we synthesized viscoelastic conjugated polythiophene P3ODT featuring branched alkyl side chains and blended with linear-side-chain P3OT. The resulting blends were further doped by the molecular dopant F<sub>4</sub>-TCNQ, to fabricate flexible thermoelectric materials. Crucially, P3ODT incorporation mitigated film degradation by suppressing phase separation, yet simultaneously reduced conductive complex formation and crystallinity while increasing structural disorder. Although F<sub>4</sub>-TCNQ effectively generated polaron/bipolaron in P3OT, its doping efficiency in P3ODT was limited due to steric hindrance from bulky side chains. Optimized thermoelectric performance emerged at P3ODT:P3OT=1:9, achieving a peak power factor of 0.697  $\mu\text{W m}^{-1}\text{K}^{-2}$ . This balance originated from dual role of P3ODT: its alkyl side chains enhanced carrier mobility through backbone planarization, compensating for reduced carrier concentration and conductivity. Thus, blending of a second conjugated polymer with tailored side chains represents an effective strategy for enhancing thermoelectric





properties in flexible organic materials, providing new molecular design principles for performance optimization.

## Author contributions

We strongly encourage authors to include author contributions and recommend using [CRediT](#) for standardised contribution descriptions. Please refer to our general [author guidelines](#) for more information about authorship.

## Conflicts of interest

In accordance with our policy on [Conflicts of interest](#) please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that "There are no conflicts to declare".

## Data availability

A data availability statement (DAS) is required to be submitted alongside all articles. Please read our [full guidance on data availability statements](#) for more details and examples of suitable statements you can use.

## Acknowledgements

We are grateful for the financial support provided by National Natural Science Foundation of China (grant no. 52173175), the Project of Key Laboratory of General Universities in Guangdong Province (No. 2023KSYS007).

## References

- 1 T. A. Yemata, Y. Zheng, A. Kyaw, X. Z. Wang, J. Song, W. S. Chin and J. W. Xu, *FRONTIERS IN CHEMISTRY*, 2020, 7, 870.
- 2 J. S. Liang, J. Liu, P. F. Qiu, C. Ming, Z. Y. Zhou, Z. Q. Gao, K. P. Zhao, L. D. Chen and X. Shi, *Nat. Commun.*, 2023, 14, 8442.
- 3 X. H. Chen, Z. Q. Gao, P. F. Qiu, W. W. Zheng, T. R. Wei, L. D. Chen and X. Shi, *Adv. Funct. Mater.*, 2025.
- 4 Z. Fan, Y. Y. Zhang, L. J. Pan, J. Y. Ouyang and Q. Zhang, *Renew. Sust. Energ. Rev.*, 2021, 137, 110448.
- 5 O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren and X. Crispin, *Nat. Mater.*, 2011, 10, 429-433.
- 6 J. L. BREDAS and G. B. STREET, *Accounts Chem. Res.*, 1985, 18, 309-315.
- 7 B. Tsuie, J. L. Reddinger, G. A. Sotzing, J. Soloducho, A. R. Katritzky and J. R. Reynolds, *JOURNAL OF MATERIALS CHEMISTRY*, 1999, 9, 2189-2200.
- 8 S. Masoumi, S. O'Shaughnessy and A. Pakdel, *Nano Energy*, 2022, 92, 106774.
- 9 S. H. Cho, J. W. Ha, C. E. Song, Y. H. Kang, M. J. Han, S. Lee and B. Park, *Chem. Eng. J.*, 2025, 508.
- 10 X. L. Zhong, Y. L. Qiao, Q. J. Yin, Y. H. Wang and G. Zhou, *Compos. Interface.*, 2025, 32, 1033-1052.
- 11 A. Lis, K. Zazakowny, K. Wolski, S. Zapotoczny and K. T. Wojciechowski, *Chem. Eng. J.*, 2025, 515.
- 12 Z. J. Chen, Y. Wen, Y. C. Xu, D. N. Li, Q. J. Le, S. Shin and J. Y. Ouyang, *Adv. Funct. Mater.*, 2025, 35. DOI: 10.1039/D5LP00223K
- 13 D. L. Meyer, N. Schmidt-Meinzer, C. Matt, S. Rein, F. Lombeck, M. Sommer and T. Biskup, *J. Phys. Chem. C*, 2019, 123, 20071-20083.
- 14 F. Zhong, Y. Y. Zheng, J. Song, L. D. Chen and H. Li, *Adv. Funct. Mater.*, 2025.
- 15 H. Kim, S. B. Kim, S. Pyo, J. Jang and I. H. Jung, *Adv. Funct. Mater.*, 2025, 35.
- 16 A. Shinohara, C. J. Pan, Z. F. Guo, L. Y. Zhou, Z. H. Liu, L. Du, Z. C. Yan, F. J. Stadler, L. Wang and T. Nakanishi, *Angew. Chem. Int. Edit.*, 2019, 58, 9581-9585.
- 17 Z. F. Guo, A. Shinohara, C. J. Pan, F. J. Stadler, Z. H. Liu, Z. C. Yan, J. L. Zhao, L. Wang and T. Nakanishi, *MATERIALS HORIZONS*, 2020, 7, 1421-1426.
- 18 T. J. Aubry, J. C. Axtell, V. M. Basile, K. J. Winchell, J. R. Lindemuth, T. M. Porter, J. Y. Liu, A. N. Alexandrova, C. P. Kubiak and S. H. Tolbert, *Adv. Mater.*, 2019, 31, 1805641-1805647.
- 19 V. I. Arkhipov, P. Heremans, E. V. Emelianova, G. J. Adriaenssens and H. Bässler, *Appl. Phys. Lett.*, 2003, 82, 3245-3247.
- 20 A. M. Glauddell, J. E. Cochran, S. N. Patel and M. L. Chabiny, *Adv. Energy Mater.*, 2015, 5, 1041072.
- 21 C. C. Wang, D. T. Duong, K. Vandewal, J. Rivnay and A. Salleo, *PHYSICAL REVIEW B*, 2015, 91, 085205.
- 22 H. Méndez, G. Heimel, S. Winkler, J. Frisch, A. Opitz, K. Sauer, B. Wegner, M. Oehzelt, C. Röthel, S. Duhm, D. Többsens, N. Koch and I. Salzmann, *Nat. Commun.*, 2015, 6, 8560.
- 23 D. Kiefer, R. Kroon, A. I. Hofmann, H. D. Sun, X. J. Liu, A. Giovannitti, D. Stegerer, A. Cano, J. Hynynen, L. Y. Yu, Y. D. Zhang, D. Q. Nai, T. F. Harrelson, M. Sommer, A. J. Moulé, M. Kemerink, S. R. Marder, I. McCulloch, M. Fahlman, S. Fabiano and C. Muller, *Nat. Mater.*, 2019, 18, 149.
- 24 D. T. Scholes, S. A. Hawks, P. Y. Yee, H. Wu, J. R. Lindemuth, S. H. Tolbert and B. J. Schwartz, *J. Phys. Chem. Lett.*, 2015, 6, 4786-4793.
- 25 S. N. Patel, A. M. Glauddell, K. A. Peterson, E. M. Thomas, K. A. O'Hara, E. Lim and M. L. Chabiny, *SCIENCE ADVANCES*, 2017, 3, 1700434.
- 26 H. Martens, I. N. Hulea, I. Romijn, H. B. Brom, W. F. Pasveer and M. Michels, *PHYSICAL REVIEW B*, 2003, 67, 121203.
- 27 G. Z. Zuo, X. J. Liu, M. Fahlman and M. Kemerink, *Adv. Funct. Mater.*, 2018, 28, 1703280.
- 28 P. Pingel and D. Neher, *PHYSICAL REVIEW B*, 2013, 87.
- 29 H. Hase, K. O'Neill, J. Frisch, A. Opitz, N. Koch and I. Salzmann, *J. Phys. Chem. C*, 2018, 122, 25893-25899.
- 30 N. Saxena, J. Keilhofer, A. K. Maurya, G. Fortunato, J. Overbeck and P. Müller-Buschbaum, *ACS APPLIED ENERGY MATERIALS*, 2018, 1, 336-342.
- 31 Z. Fan, D. G. Du, H. Y. Yao and J. Y. Ouyang, *ACS Appl. Mater. Inter.*, 2017, 9, 11732-11738.
- 32 K. Kang, S. Watanabe, K. Broch, A. Sepe, A. Brown, I. Nasrallah, M. Nikolka, Z. P. Fei, M. Heeney, D. Matsumoto, K. Marumoto, H. Tanaka, S. Kuroda and H. Sirringhaus, *Nat. Mater.*, 2016, 15, 896.
- 33 A. J. Tang, Y. P. Li, R. Wang, J. W. Yang, C. Q. Ma, Z. Li, Q. Zou and H. X. Li, *Chem. Commun.*, 2023, 59, 1305-1308.
- 34 L. Ma, P. Hu, H. Jiang, C. Kloc, H. D. Sun, C. Soci, A. A. Voityuk, M. E. Michel-Beyerle and G. G. Gurzadyan, *Sci. Rep.-UK*, 2016, 6, 28510.
- 35 M. Ziat, N. Bekkioui and H. Ez-Zahraouy, *J. Phys. Chem. Solids*, 2022, 161, 110409.
- 36 Y. Zhang, Q. Yang, C. Lin, R. J. Chen, S. R. Maliha, Y. Chen, J. J. Xu





## ARTICLE

## Journal Name

and C. J. Pan, *J. Mater. Chem. A*, 2024, 12, 29262-29270.

View Article Online  
DOI: 10.1039/D5LP00223K

Open Access Article. Published on 22 September 2025. Downloaded on 9/24/2025 4:53:08 AM.  
This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.



RSC Applied Polymers Accepted Manuscript

## Data Availability Statement

Data for “Electrical and Thermoelectric Properties of a Poly(3-(2-octyldodecyl)thiophene)/Poly(3-octylthiophene)/2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane Viscoelastic Polymer Blend Doping System” is available in article supplementary information.

Authors: Roujun Chen,<sup>a,b</sup> Zijian Yin<sup>a</sup>, Zhongming Chen<sup>c,\*</sup>, and Chengjun Pan<sup>a,\*</sup>

